



GSFC • 2015

An Introduction to Atomic Layer Deposition with Thermal Applications

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NASA GSFC Code 545**



What is a Thin Film?

Thin film: thickness typically $<1000\text{nm}$.

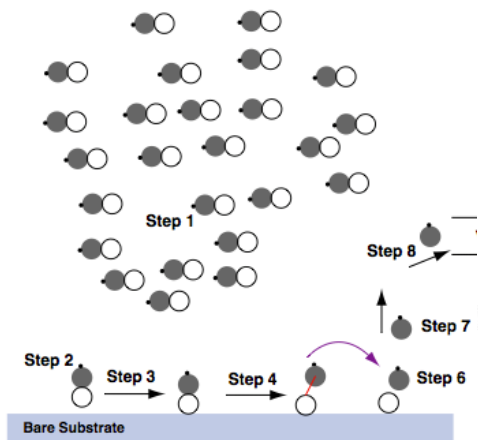
Special properties of thin films: different from bulk materials, it may be –

- Not fully dense
- Under stress
- Different defect structures from bulk
- Quasi - two dimensional (very thin films)
- Strongly influenced by surface and interface effects

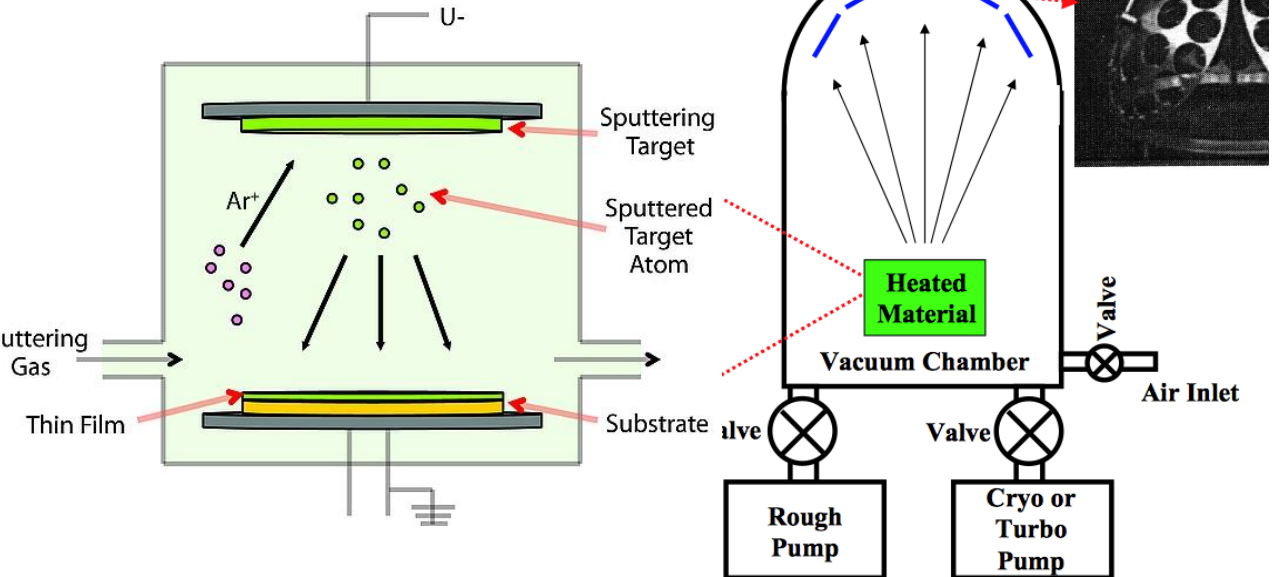


Other Deposition Techniques

CVD Process



1. Precursor gas phase reaction
2. Diffusion
3. Adsorption
4. Surface Process
5. Desorption
6. Diffusion
7. Purge

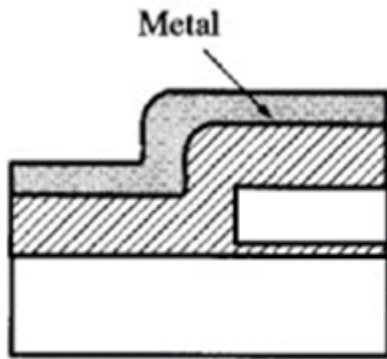




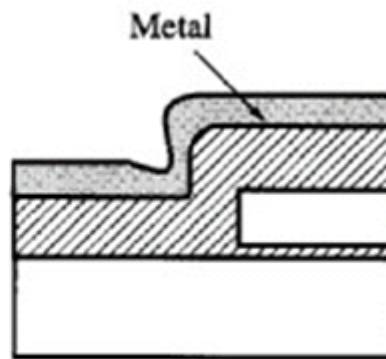
Common Denominator

- Deposition only occurs on substrates that “see” the target.
- Plasma process can damage the substrate
- Poor thickness control
- Poor Step Control
- High Pressure High Temperature Environment

Step Coverage Example

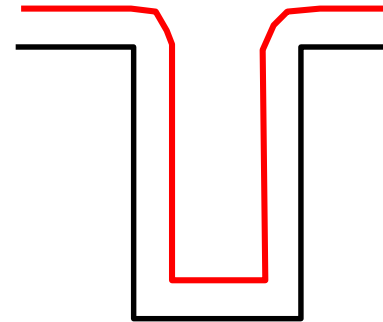


(a)

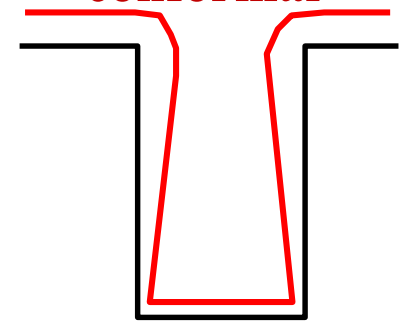


(b)

conformal



non-conformal



Step coverage of metal over non-planar topography.

(a) Conformal step coverage, with constant thickness on horizontal and vertical surfaces.

(b) Poor step coverage, here thinner for vertical surfaces.



Introduction

Atomic Layer Deposition



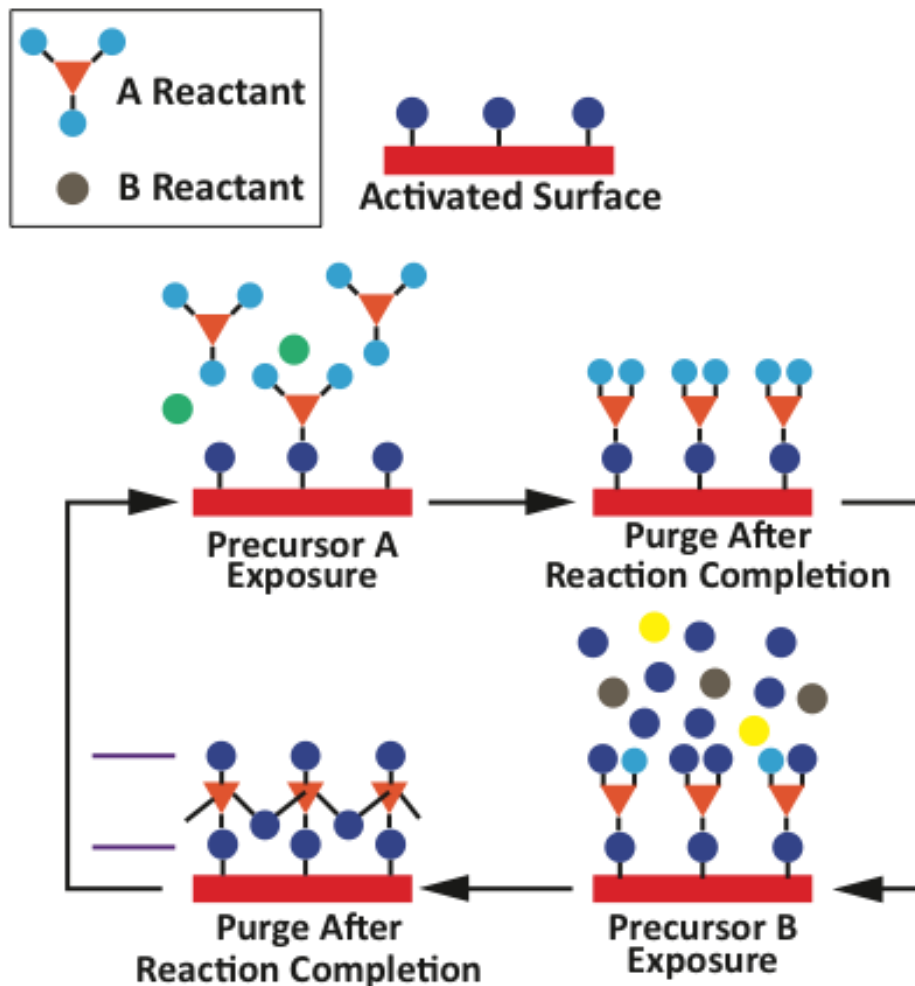
A thin film “nanomanufacturing” tool that allows for the conformal coating materials on a myriad of surfaces with precise atomic thickness control.

Based on:

- **Paired gas surface reaction chemistries**
- **Benign non-destructive temperature and pressure environment**
 - **Room temperature -> 250 °C (even lower around 45 °C)**
 - **Vacuum**



ALD Procedure



- **A or B exposure = Half Cycle**
- **A+B = Full Cycle = 1 Monolayer**
- **Digital Process: ABABABAB**
- **Not Line of Sight, EVERYTHING GETS COATED**
- **Substrate Independent**



Periodic Table of ALD Films

H 1																	He 2														
<div>O</div> Li 3	Be 4																	<div>O</div> <div>N</div> B 5	<div>C</div> C 6	<div>N</div> N 7	<div>O</div> O 8	<div>F</div> F 9	Ne 10								
Na 11	<div>O</div> Mg 12 F																	<div>O</div> <div>N</div> <div>M</div> <div>P</div> Al 13	<div>O</div> <div>N</div> <div>M</div> Si 14	P 15	S 16	Cl 17	Ar 18								
K 19	<div>O</div> Ca 20 F	<div>O</div> Sc 21	<div>O</div> <div>N</div> <div>M</div> Ti 22 S	<div>O</div> V 23	<div>O</div> Cr 24	<div>O</div> <div>N</div> <div>M</div> Mn 25 S D	<div>O</div> <div>N</div> <div>M</div> Fe 26	<div>O</div> <div>N</div> <div>M</div> Co 27	<div>O</div> <div>N</div> <div>M</div> Ni 28	<div>O</div> <div>N</div> <div>M</div> Cu 29 S D	<div>O</div> <div>N</div> <div>M</div> Zn 30 F D	<div>O</div> <div>N</div> <div>M</div> Ga 31 P D	<div>O</div> <div>N</div> <div>M</div> Ge 32	As 33	Se 34	Br 35	Kr 36														
Rb 37	<div>O</div> Sr 38 F	<div>O</div> Y 39	<div>O</div> <div>N</div> Zr 40	<div>O</div> <div>N</div> Nb 41	<div>O</div> <div>N</div> <div>M</div> Mo 42	Tc 43	<div>O</div> <div>M</div> Ru 44	<div>O</div> <div>M</div> Rh 45	<div>O</div> <div>M</div> Pd 46	<div>O</div> <div>M</div> Ag 47	<div>O</div> <div>M</div> Cd 48	<div>O</div> <div>N</div> <div>M</div> In 49 P S	<div>O</div> <div>N</div> <div>M</div> Sn 50 S D	<div>O</div> <div>M</div> Sb 51 D	Te 52	I 53	Xe 54														
Cs 55	<div>O</div> Ba 56 S	<div>O</div> La 57 F	<div>O</div> <div>N</div> <div>M</div> Hf 72 F S C	<div>O</div> <div>N</div> <div>M</div> Ta 73	<div>O</div> <div>N</div> <div>M</div> W 74	<div>O</div> Re 75	<div>O</div> Os 76	<div>O</div> <div>M</div> Ir 77	<div>O</div> <div>M</div> Pt 78	Au 79	Hg 80 S	Tl 81	<div>O</div> <div>S</div> <div>D</div> Pb 82	<div>O</div> Bi 83	Po 84	At 85	Rn 86														
Fr 87	Ra 88	Ac 89	Rf 104	Db 105	Sg 106	Bh 107	Hs 108	Mt 109																							
																		<div>O</div> <div>D</div> Ce 58	<div>O</div> Pr 59	Nd 60	Pm 61	<div>O</div> Sm 62	<div>O</div> <div>D</div> Eu 63	<div>O</div> Gd 64	<div>O</div> <div>D</div> Tb 65	<div>O</div> Dy 66	<div>O</div> Ho 67	<div>O</div> <div>N</div> <div>M</div> Er 68	<div>O</div> <div>D</div> Tm 69	<div>O</div> Yb 70	<div>O</div> Lu 71
																		Th 90	Pa 92	U 93	Np 94	Pu 95	Am 96	Cm 97	Bk 98	Cf 100	Es 101	Fm 102	Md 104	No 4	Lr 4

O

:Oxide
N:Nitride
M:Metal
P:Phosphide/Asenide
S:Sulphide/Selenide/Telluride

C

:Carbide
F:Fluoride
D:Dopant

O

 Oxide of this element has been deposited by the ALD community

O

 Recipe for this material is available from CNT staff or customer base

Acknowledgements

- Gordon, Roy (2008). Atomic Layer Deposition (ALD): An Enable for Nanoscience and Nanotechnology. PowerPoint lecture presented at Harvard University, Cambridge, MA.
- Elam, Jeffrey (2007). ALD Thin Film Materials. Argonne National Laboratory



Advantageous Property

Precise Thickness Control

Thickness = \mathcal{F} (# monolayers)

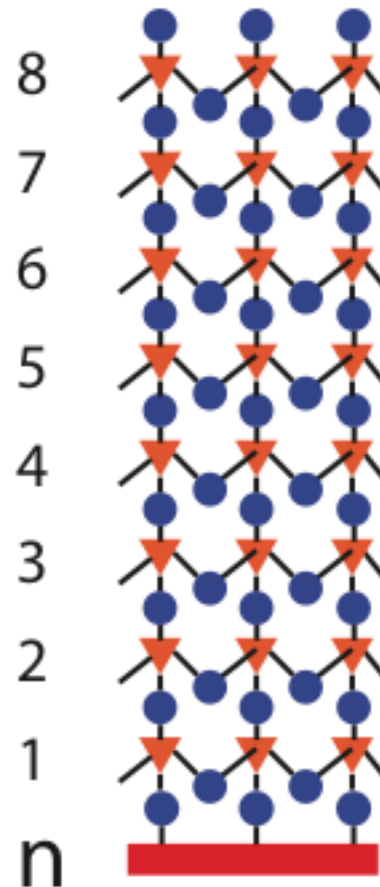
Example:

If 1 monolayer = 1 Å

monolayers = 7

Thickness = 7 Å

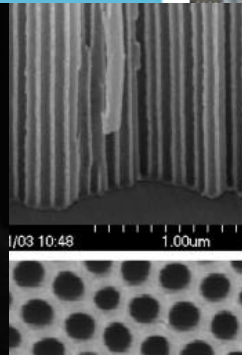
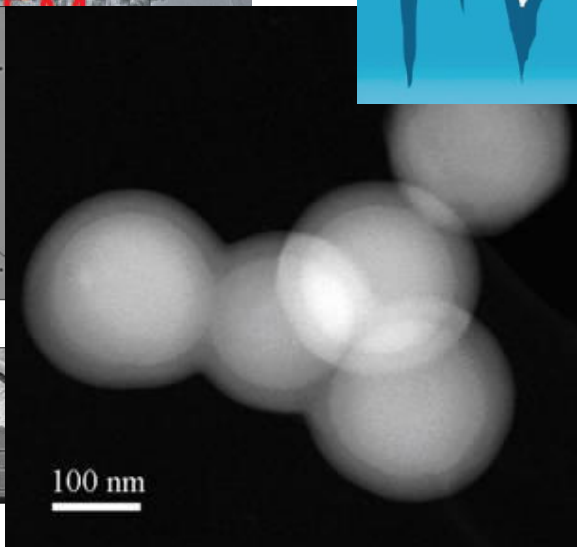
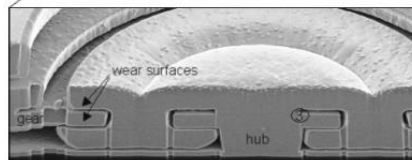
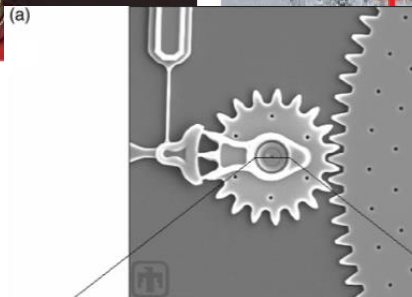
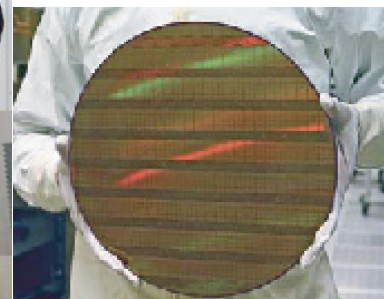
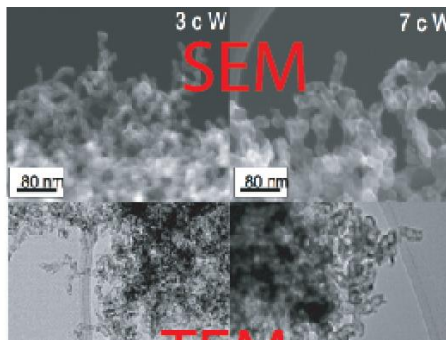
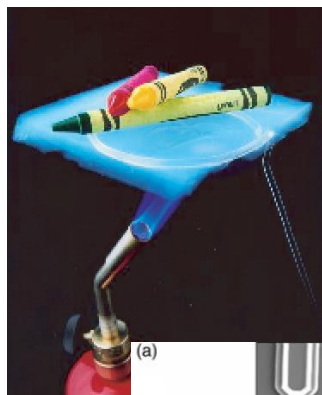
Reproducibility





Advantageous Property

Substrate Independence

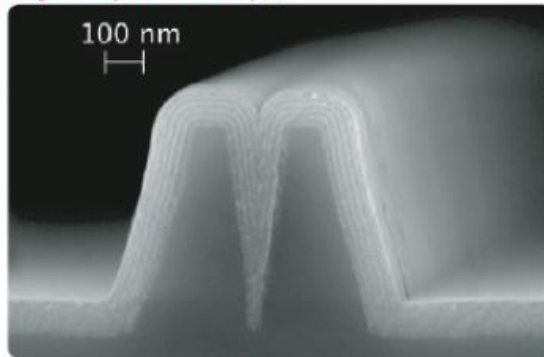




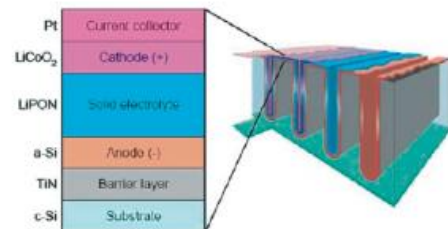
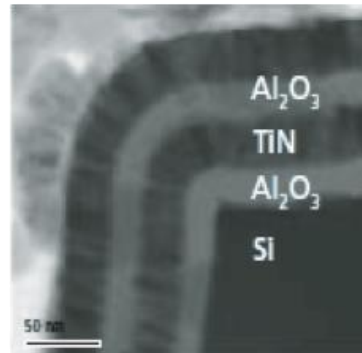
Advantageous Property

Epitaxial Growth

Artificial trench filled with an ALD nanolaminate
Image courtesy of Aalto University (FI)



Multilayer consisting of:
Al₂O₃ - 25 nm
TiN - 20 nm
Al₂O₃ - 25 nm
Dr. Fred Roozeboom, NXP Semiconductors Research and
Dr. Erwin Kessels, University of Technology, Eindhoven

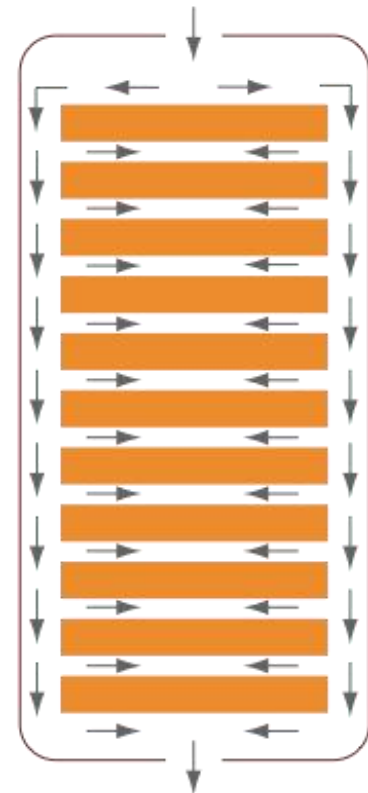


Schematic of a 3D battery integrated in a Si-substrate.
The cross-section shows the various functional layers
in the battery stack as well as the candidate materials.
Knoops, H.C.M. et al., ECS Trans., 25 (2009) pp. 333-344

Batch Process



Coating Silver with Aluminum Oxide
<http://www.glassonweb.com/>





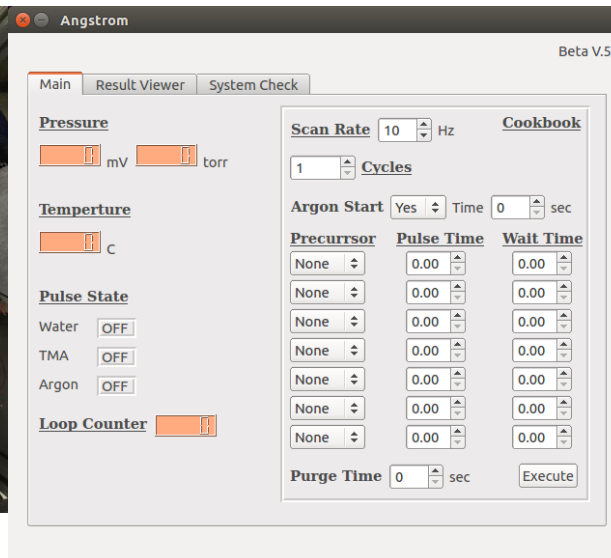
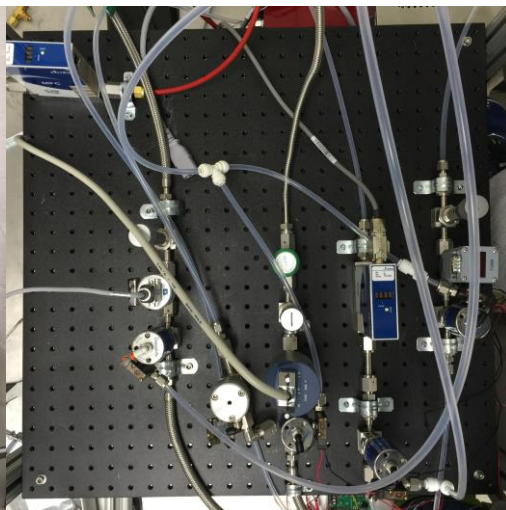
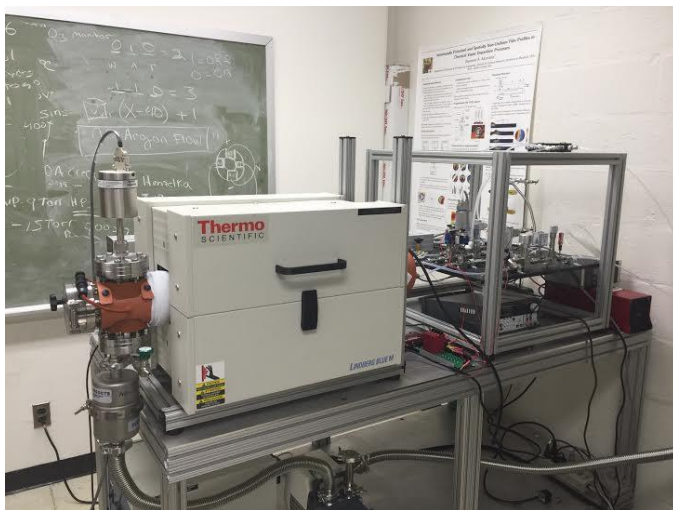
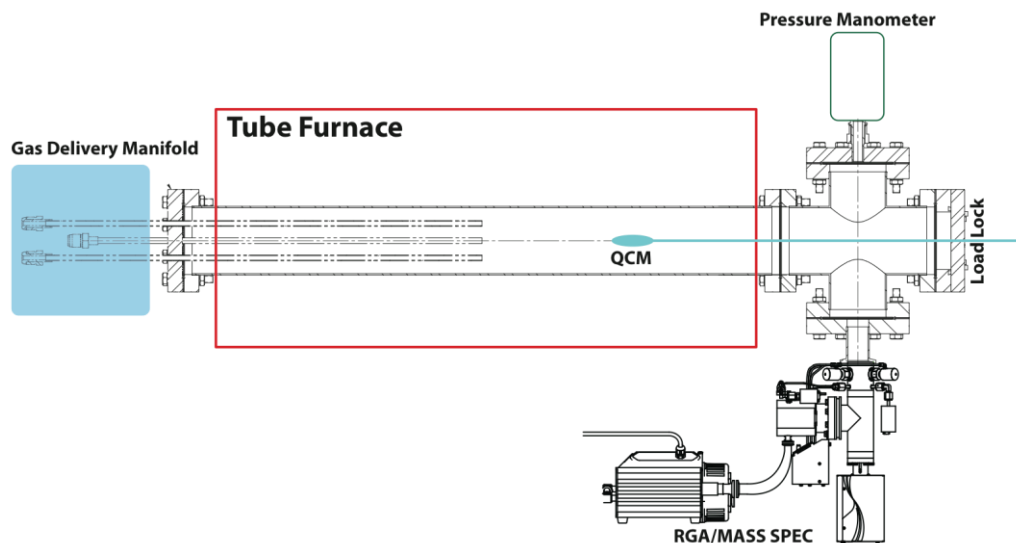
Building off a Commercial Reactor

Commercial Options



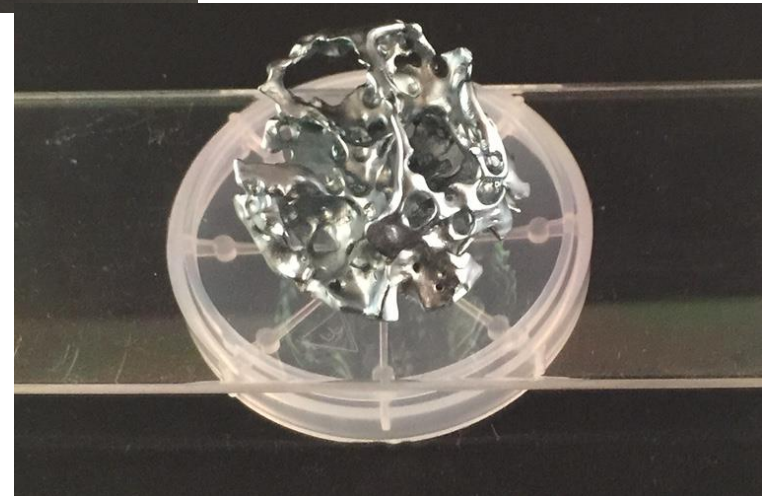
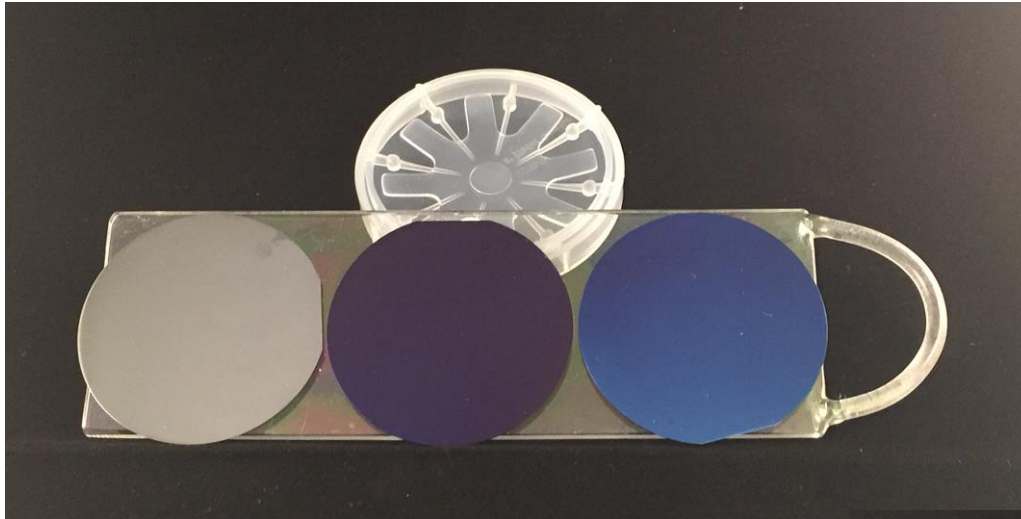


In-House Experimental ALD System



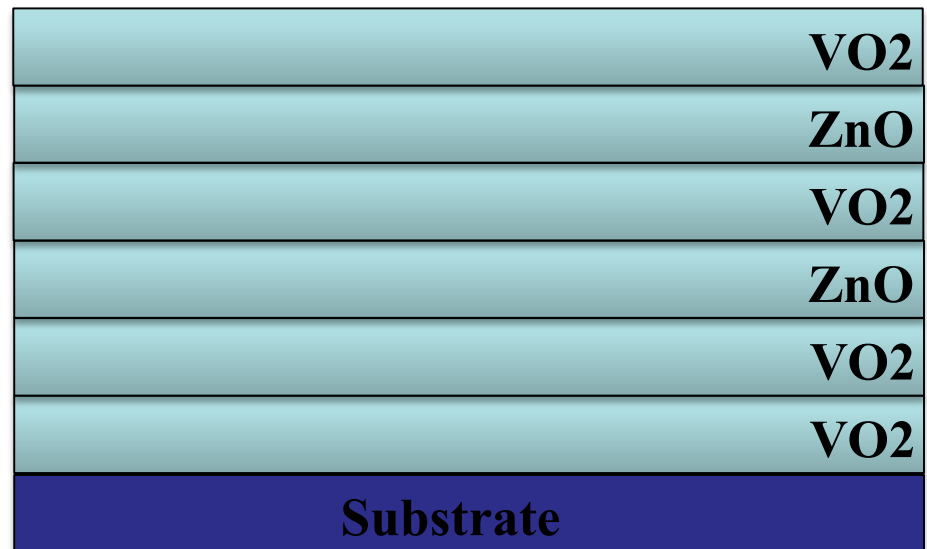
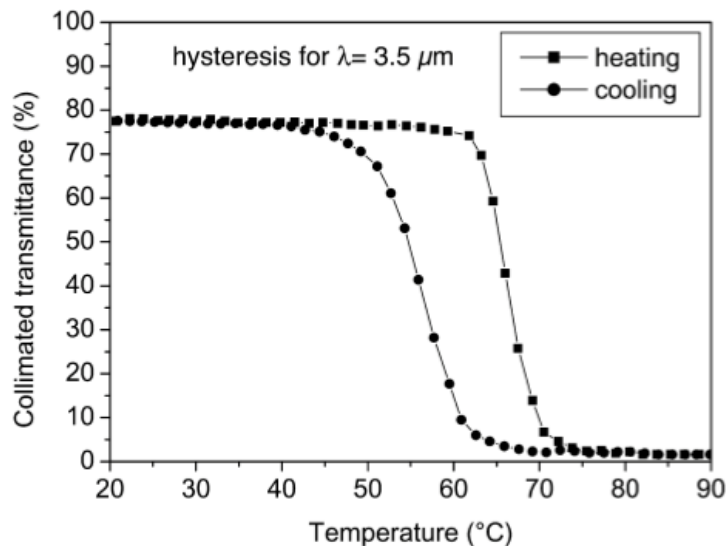
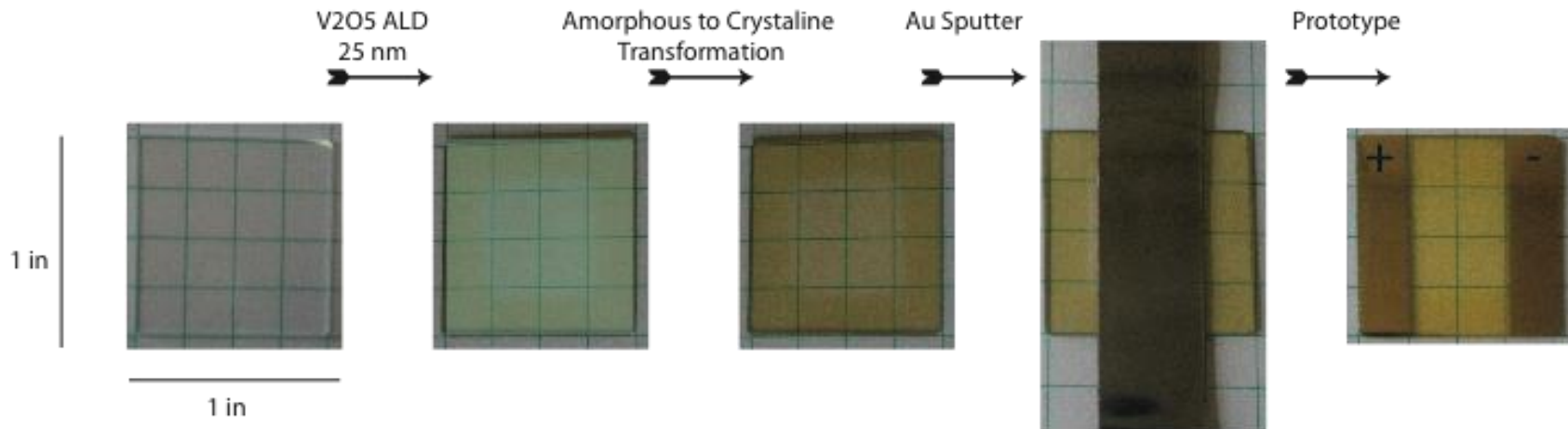


Thermal Applications and Results





Passive Thermal Films





ZnO

$E = hc/\lambda$ where:

f = frequency in Hertz ($\text{Hz} = 1/\text{sec}$)

λ = wavelength in meters (m)

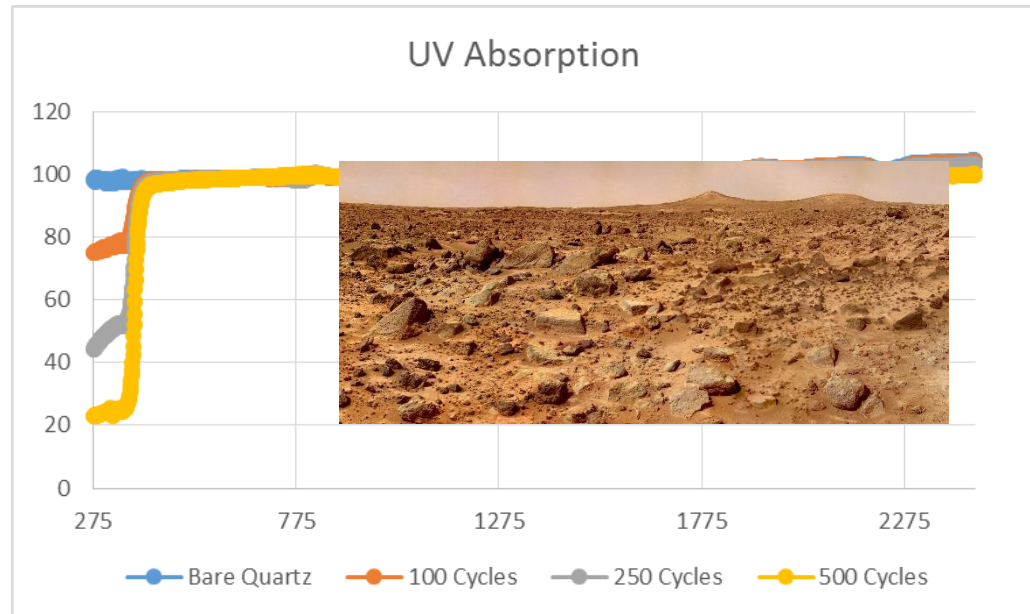
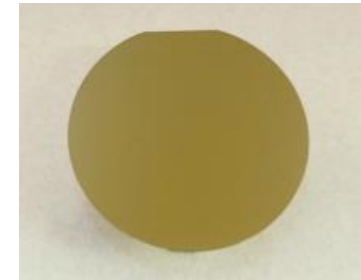
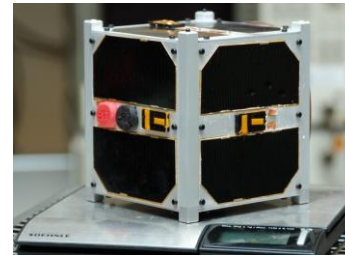
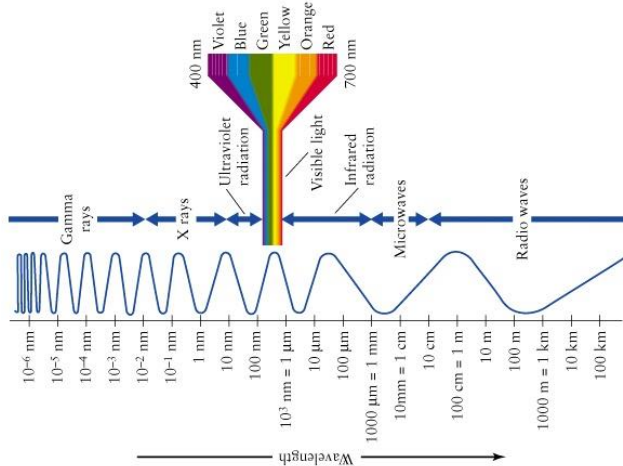
c = the speed of light (299792458 m/s)

E = energy in electron Volts (eV)

h = Planck's constant ($6.626068 \times 10^{-34} \text{ m}^2\text{kg/s}$)

$E_{\text{ZnO}} = 3.3 \text{ eV}$

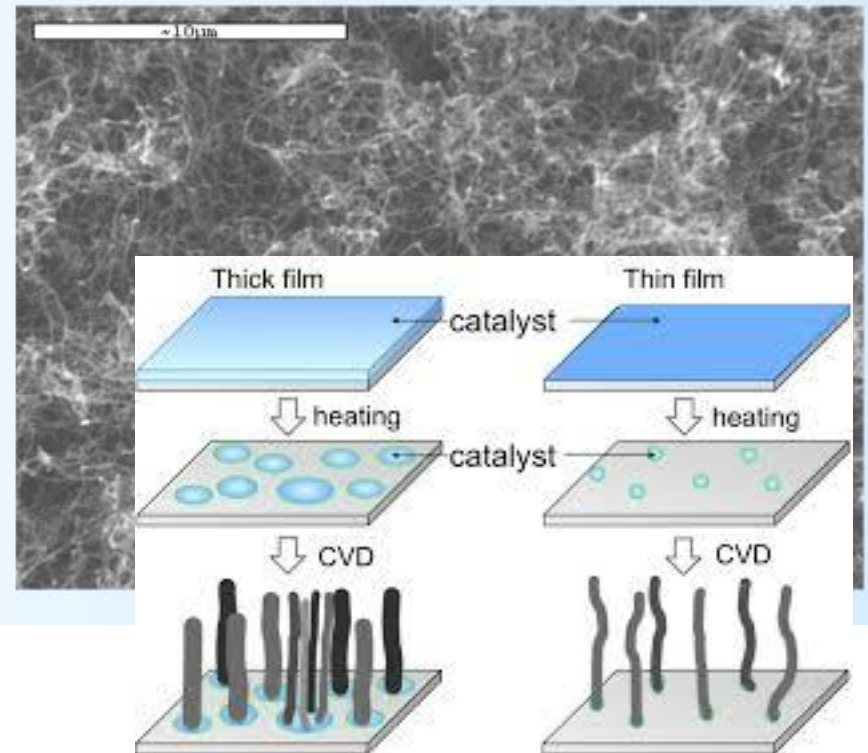
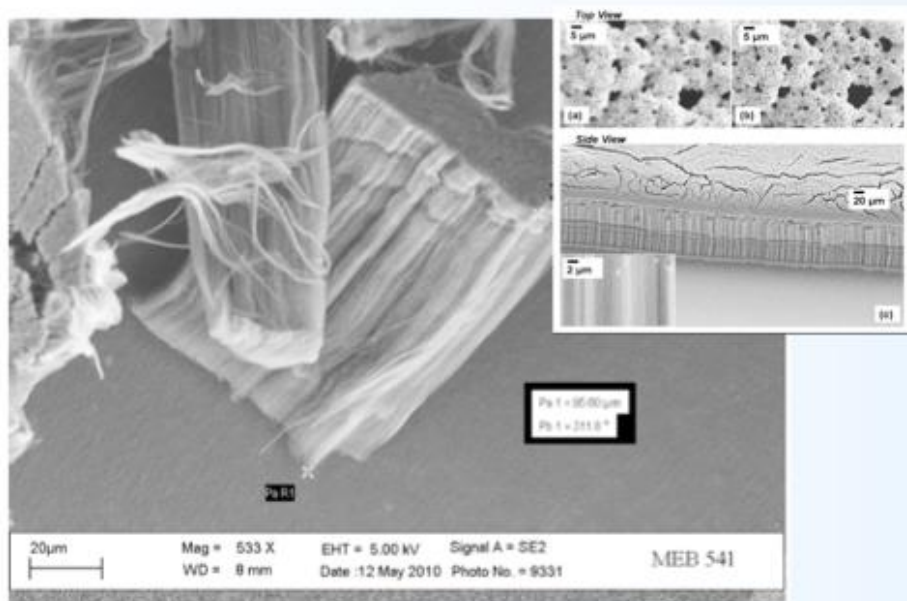
$\lambda_{\text{ZnO}} \sim 375 \text{ nm}$





Blacker Than Black Carbon Nanotubes

Fe ALD on Complex Geometries for Carbon Nanotube Growth



Substrate + Catalyst + Gas = CNNT
Si,Ti, flat, 3d + Iron + Ethylene

Blacker than NASA Z306 Paint 10X Darker



Atomic Oxygen Protection



100 nm on Kapton

1000 Cycles

155 °C

Al_2O_3

**GPM Funded an experiment
at Glenn to determine AO effects
on materials.**

**99% mass retention after a simulated
5 year flux**



Questions?

